

Treatment of wastes containing cesium ions by electrochemical ion-exchange (EIX)

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In this study, an electrochemical ion-exchange (EIX) technique, based on cationic resin and zirconium phosphate (ZrP), have been chosen for the separation of cesium from radioactive wastes. These materials show high chemical stability in oxidizing media and under ionizing radiation. Charcoal, graphite and binder used in the formulation of electrodes have been studied as well. 99.8% of the cesium sorption from solution was observed. The great advantage of this process is the total release of cesium at room temperature, by reversing polarities, which makes possible the reuse of the electrode without losing its exchanging capacity.

Introduction

Nowadays, environmental preservation using clean technologies, generating non-toxic residues and reducing volumes, is important. Electrochemical ion-exchange (EIX) is an advanced process that has advantages over the traditional ion-exchange because of the use of electrons as the only reagent.

In the present work, a separation process which separates cesium from radioactive waste has been studied, using electrochemical ion-exchange technique. The reason for developing this kind of process, which uses electrochemistry as a primary tool, comes from environmental preservation concerns. EIX is an advanced process that has advantages over the traditional ion-exchange and the fact of using electrons as the only “reagent”, reduces the volume of the solution to be treated. The ion-exchange electrode is prepared by a mixture of an ion-exchanger, an electric conductor and a binder.

In this study, cationic resin Amberlite CG-50 has been chosen for the separation of cesium from waste. The quantities of charcoal, graphite and binder used in the formulation of the electrodes have been studied. The great advantages of this process are the total elution of cesium, without addition of reagents and the possible reuse of the electrode without losing its exchanging capacity.

Electrochemical ion-exchange is an advanced ion-exchange process. The ion-exchanger can be incorporated in the electrode structure with a binder.

Weak acid cationic exchangers are not good adsorbers in neutral pHs but require a more basic media to produce the necessary adsorption active sites for ion-exchange. The electrochemical adsorption solves this problem by generating an alkaline media next to the electrode.^{1,2,9,11}

The main advantage of this process is that the ion-exchanger can be desorbed without adding chemicals, which allows the regeneration and reuse of ion-exchange material.⁵

EVANS^{2,3,4} showed that the electrode manufacturing is an “art” because particle sizes and the chemical nature of the resin are very important, since they can dramatically change the results. The main considerations when choosing electrode materials for EIX are its performance characteristics and its degradation resistance.

In this work EIX electrodes for cesium adsorption have been developed. Cesium is usually found in irradiated fuel treatment solutions and is responsible for the high activity of this waste. The chosen ion-exchanger was zirconium phosphate (ZrP), due to its stability to high radiation exposure, temperature and pH variation.

Experimental

The radioactive tracer technique was chosen in this work. The solution of ¹³⁴Cs in 0.1 mol·L⁻¹ HNO₃ was prepared from a cesium chloride solution and was analyzed by gamma-spectrometry, using a NaI detector. The energy peak used to control the gamma-emission was 604.7 keV. In all experiments the radioactive concentration of cesium in the solution was 2.33·10⁻⁵ Bq·mL⁻¹.

Several electrodes have been developed by varying the quantities of the materials. Besides zirconium phosphate, which was prepared in our laboratory,^{6,7} some others material were selected such as: (a) graphite powder, used to increase electrode electrical conductivity and guarantee a uniform distribution for electrical potential; (b) Norit A[®] charcoal, used to increase electrode sorption, because it helps in hydrogen

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ion adsorption and active sites formation; (c) Kraton 1101[®], a double-blocked co-polymer of styrene and butadiene, which was dissolved in toluene 1:10, to act as a binder for electrode components; and (d) carbon felt used as a current feeder, which also shows a good adhesive property when applied in the electrode mass, good electrical conductivity, good work media resistance and some flexibility after electrode manufacturing, what makes the cell handling easier.

Charcoal and graphite powder were added during the synthesis of ZrP. The procedure of ZrP ion-exchanger

preparation was as described in References 6 and 7. Figure 1 shows the photo of the grain obtained from this preparation and Fig. 2 shows its surface profile. This powder was mixed with the binder previously dissolved in toluene 1:10. The final product, a viscous liquid, was applied to a carbon felt and it was let to dry for one hour at room temperature. Two more layers were applied to the carbon felt with one hour interval between each of them. The same procedure was applied to the other side of the carbon felt. The electrode size was 1.0 cm².

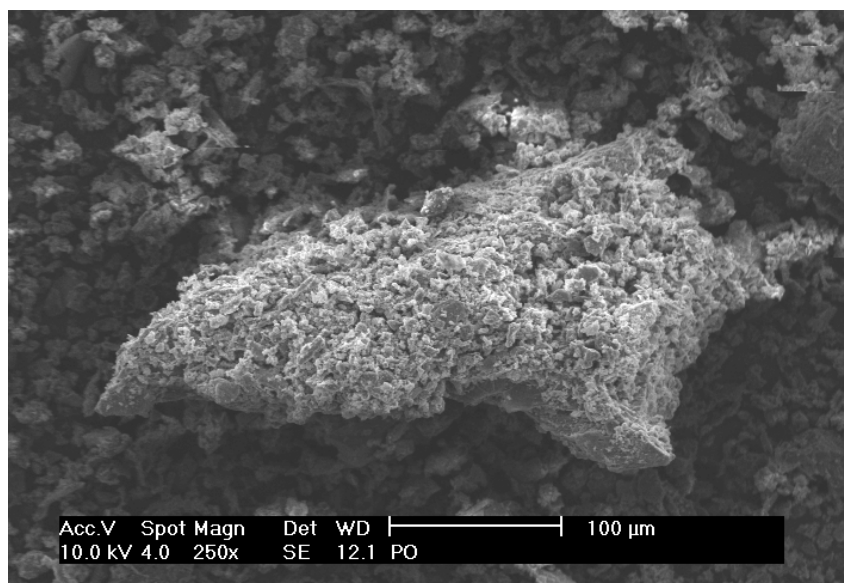


Fig. 1. Photomicrograph of a grain of zirconium phosphate with charcoal and graphite powder, ×500 times

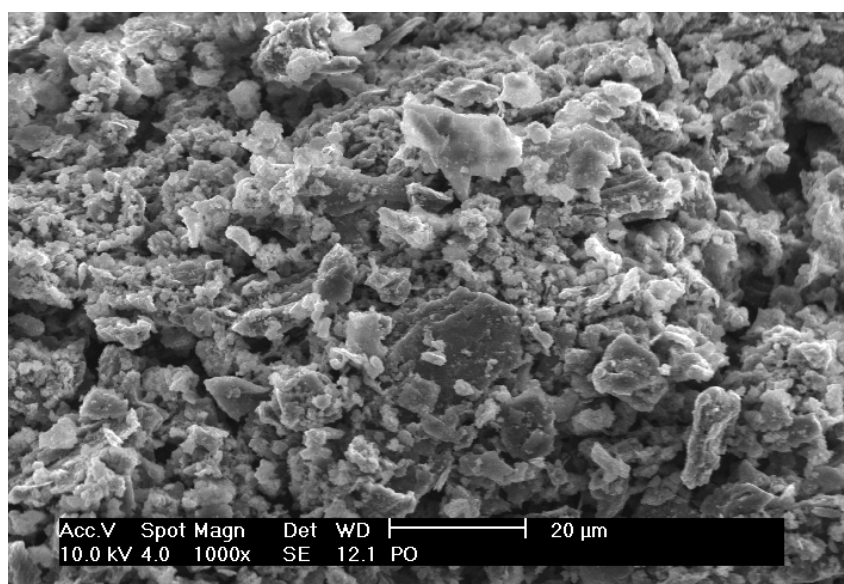


Fig. 2. Surface photomicrograph of the grain of zirconium phosphate with charcoal and graphite powder, ×1000 times

The experiments were carried out in a jacketed three-electrode cell, using Ag/AgCl as the reference electrode, a platinum plate as counter electrode and the electrochemical ion exchanger as the working electrode. Electrochemical measurements were performed using an AUTOLAB (Model PGSTAT 30) potentiostat/galvanostat coupled to a personal computer with GPES software.

Results and discussion

The working electrode potential for cesium sorption was chosen by measuring the time necessary to increase the pH in the electrolyte. This fact generates ideal conditions for the production of active sites in the ZrP ion-exchanger, which is a necessary condition for ion-exchange. Several measures were made from 0.500 V (vs. Ag/AgCl) to more negative potentials, until hydrogen evolution was achieved, which occurred at -1.0 V (vs. Ag/AgCl). The -0.250 V (vs. Ag/AgCl) potential was chosen because it caused a fast pH increase in the medium. When more negative potentials were tested, no significant difference was observed, in comparison to the chosen one. Further more, the -0.250 V (vs. Ag/AgCl) potential is far from hydrogen evolution potential, what could interfere in the EIX process.

The experiments were carried out in triplicate for each electrode formulation, except for the electrodes that disintegrated during the process.

Thirty electrodes were manufactured, varying the weight percentages of the components. Table 1 shows the twelve electrode formulations that were chosen as significant for the experiment.

It was found that the maximum binder percentage was 25%, because above this value the electrode capacity decreased as shown in the electrodes 8 and 9 in Table 1. When binder percentages below 15% were used, the electrodes did not show good mechanical properties, disintegrated as soon as the electrical potential was applied (Table 1, electrode 10). 25% w/w was chosen because the electrode presented better handling characteristics.

In the case of electrode 11 (Table 1), it was observed that below 10% graphite the current distribution starts to be compromised, which interferes in the EIX process due to decreasing the formation of active sites. On the other hand, if a percentage above 15% was used, as in

the case of electrode 5, the conductivity was good, but the lower percentage of ion-exchanger and/or charcoal leads to a decrease of the ion-exchange.

It was noticed that electrode 1 (Table 1), which was manufactured only with ZrP ion-exchanger, showed a sorption of 82.1% and electrode 2, which was only made of charcoal, showed a sorption of 68%, a lower value if compared to the first one. The combination of the ion-exchanger and the charcoal resulted in a better electrode due to the interaction between each other. Charcoal is a good H^+ adsorber, which helps to increase the pH, the necessary condition for the formation of active sites in the ion-exchanger. This interaction was observed in electrodes 3, 4 and 6 (Table 1). It was also observed that the quantity of ion-exchanger had to be equal or higher than charcoal, because when charcoal quantity is higher than the ion-exchanger, as in electrode 7, the sorption decreases.

Observing the desorption, 100% of the cesium sorbed was recovered, with little variation in time. The exception was the electrodes that presented low conductivity or were disintegrated.

The experiments have shown that the best result was the formulation of electrode 6, which had 35% of ZrP ion-exchanger, 25% of charcoal, 15% of graphite powder and 25 % of binder.

The surface of the electrode 6 can be observed in Fig. 3.

The EIX behavior was also studied by varying the temperature from room temperature to 30 °C, 45 °C and 60 °C. Few changes in the final results of sorption were noticed. At higher temperatures the sorption time was a little shorter. At room temperature, a sorption of 99.8% of cesium ion was achieved in around 4 minutes. At 30 °C there was no difference in sorption yield compared to room temperature. However, at higher temperatures the time necessary to achieve the same sorption yield decreased to around 3 minutes.

Figure 4 shows the sorption behavior of cesium.

The desorption behavior in different temperatures was also studied. It was observed that there was no significant difference in the desorption yield. At 60 °C, the time required to achieve 100% of desorption yield was 5 minutes, while at other temperatures this yield was achieved in around 6 minutes.

Figure 5 shows the desorption as a function of time. Most part of this desorption occurs in the first minute.

Table 1. Percentage of sorption and desorption of the cesium

Electrode	Weight, %	t_{ret} , min	Sorption, %	t_{elut} , min	Desorption, %	Observation
1	^a T - 70 ^b G - 15	10	82	4	100	
2	^c A - 15 C - 70 G - 15	10	68	5	100	
3	A - 15 T - 35 ^d C - 35	6	99	4	100	
4	G - 15 A - 15 T - 30 C - 30	7	99.2	4	100	
5	G - 15 A - 20 T - 25 C - 25	10	90.8	5	100	
6	G - 25 A - 25 T - 35 C - 25	4	99.8	5	100	
7	G - 15 A - 25 T - 25 C - 35	8	92	5	100	
9	G - 15 A - 25 T - 30 C - 25	10	12	8	100	
10	A - 30 T - 35 C - 30 G - 25	2	42.3	-	-	After 2 min, the electrode started to disintegrate
11	A - 10 T - 40 C - 40 G - 5	10	22.3	10	95.35	
12	A - 15 T - 30 C - 30 G - 10 A - 30	-	-	-	-	No sorption

Conditions: $[Cs] = 2.33 \cdot 10^{-5} \text{ Bq} \cdot \text{mL}^{-1}$, $[V] = -0.250 \text{ V (vs. Ag/AgCl)}$.

^a T = zirconium phosphate ion-exchanger.

^b G = graphite powder.

^c A = binder.

^d C = charcoal.

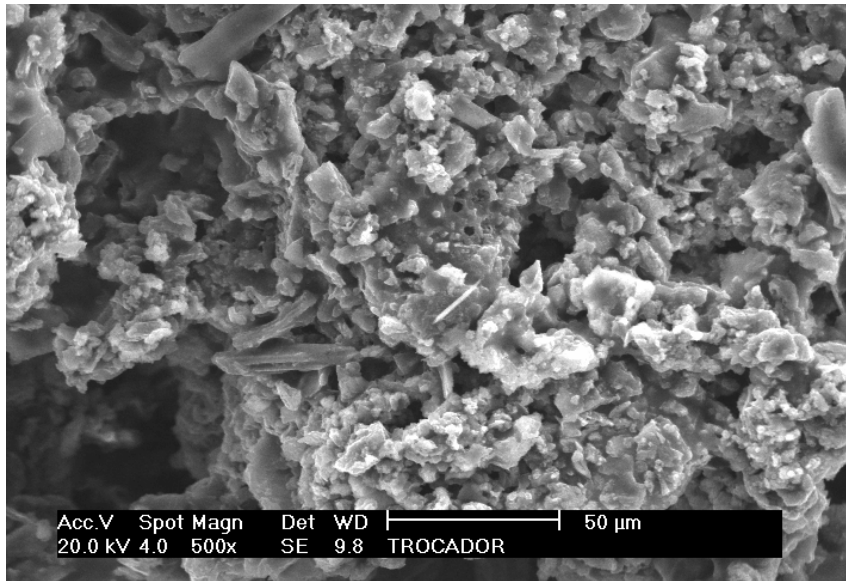


Fig. 3. Electrode photomicrography with 35% of zirconium phosphate ion-exchanger, 25% of charcoal, 15% of graphite powder and 25% of binder, $\times 500$ times

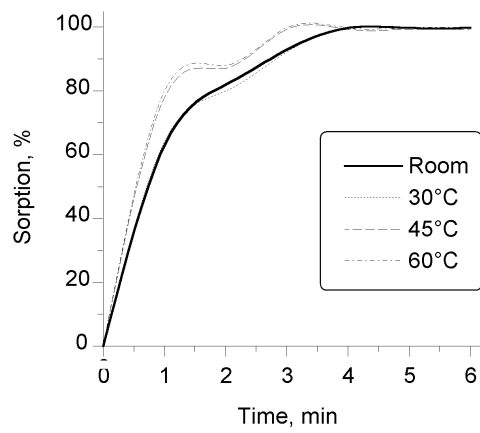


Fig. 4. Sorption curves of ^{134}Cs (feed concentration of $2.33 \cdot 10^{-5} \text{ Bq} \cdot \text{mL}^{-1}$) versus time, at different temperatures

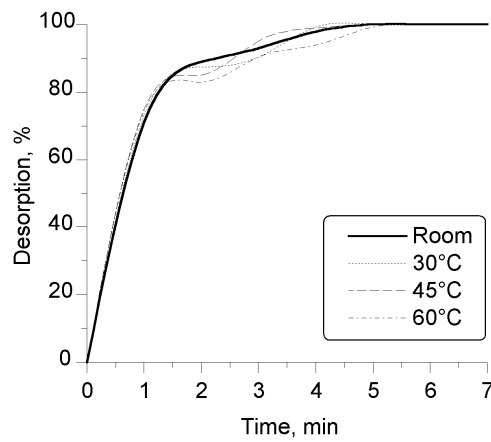


Fig. 5. Desorption curves of ^{134}Cs (feed concentration of $2.33 \cdot 10^{-5} \text{ Bq} \cdot \text{mL}^{-1}$) versus time, at different temperatures

Conclusions

The EIX process proposed in this work has shown high efficiency in treating waste containing cesium.

One of the primary advantages showed in this work was the complete desorption of the cesium ions, an important fact when compared to traditional ion-exchange process in which desorption is always lower than 100%. It makes possible the reuse of the electrode with no loss of its capacity.

The binder, graphite powder and charcoal quantities were important to produce the most efficient electrode. The binder gave better mechanical resistance, the graphite powder optimized electrode conductivity and the charcoal contributed to the adsorption process, helping in the formation of active sites.

The zirconium phosphate incorporated into the electrode has proved efficient in sorption and desorption of cesium ions at room temperature despite of studies found in the literature.

A preliminary evaluation of involved costs shows that (1) the energy consumption is low, since the required times for sorption and desorption are short and there is no need for heating because the system operates at room temperature; and (2) the materials used for electrode manufacturing have reasonable costs. In addition, the electrode can be reused many times without losing its capacity.

The photomicrograph of the best electrode (Fig. 3) showed that its surface is completely irregular, which gives a higher contact area. Because of this, the

utilization of active sites is almost complete, increasing the efficiency of the process.

One more advantage is that the small difference in the results at higher temperature, indicate that both sorption and desorption processes can be carried out at room temperature.

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